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ASSESSING THE ORIGIN OF WATER APPEARANCES IN SALT MINES

Triple Isotope Analyses (δ^2H, $\delta^{18}O$, $\delta^{17}O$) of Heavy Brines from the Klodawa Salt Mine, Central Poland

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INTRODUCTION

Polish salt deposits are situated in northern-central and southern part of Poland. They are represented either by salt domes or salt beds, usually covered by water bearing Tertiary and Quaternary formations, sometimes surrounded by older deposits. Isotope analyses of water appearances in Polish salt mines started in early the 1970s [1-3]. Soon it became clear that analyses of oxygen and hydrogen stable isotope composition of water constitutes a powerful tool for determination of the origin of mine waters and the risk assessment associated with uncontrolled water inflows.

Three major groups of water appearances in Polish salt mines can be defined:

- meteoric waters of infiltration origin, recharged during Quaternary and pre-Quaternary climates,
- syngenetic brines associated with formation of salt deposits,
- technological waters and waters of unknown origin.

While the first and third category of waters pose certain danger to the mine operation, the second category is of lesser concern because those waters are fully saturated and occur in limited quantities.

Sediments surrounding salt deposits are sources of water of meteoric origin which uncontrolled inflows may pose serious hazard to mines' operation (flooding). Chemical composition of mine waters, although useful, cannot be used to distinguish between syngenetic (safe) and meteoric (potentially dangerous) water types occurring in mines (Fig. 1).

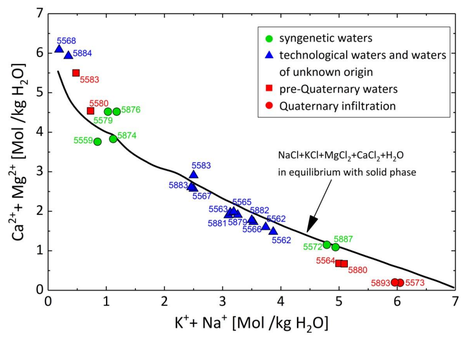


Fig. 1. Relation between the sum of Ca^{2+} + Mg^{2+} and the sum of K^+ + Na^+ cations in brine samples collected in the Klodawa Salt Mine.

STUDY AREA

The Klodawa salt deposit is situated in the central part of a 63 km long salt structure. That part pierces through the Mesozoic strata and forms a diapir 26 km long and 0.5-2 km wide (Fig. 2). The gypsum-clayey cap is at depth of 40-500 m, up to 250 m thick, and is surrounded by Quaternary and Tertiary water-bearing sediments. Below the Tertiary sediments, the diapir is surrounded by Mesozoic formations. Salt is exploited at four main levels: 450, 525, 600, 690 and 750 m and several intermediate levels. The volume of exploitation chambers is approximately 20 millions of cubic meters, with typical dimensions 120 x 12 x 12 m. Three shafts are operated. The mine is producing approximately 6×10^5 tons of salts annually.

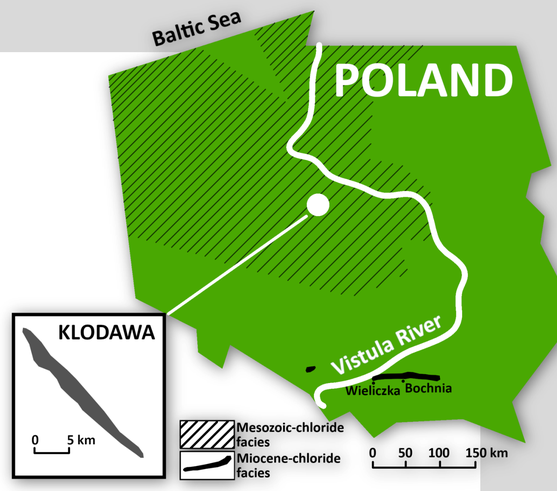
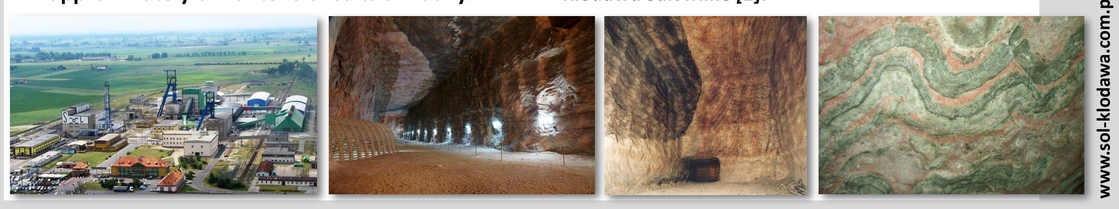


Fig. 2. Salinary provinces in Poland and location of Klodawa Salt Mine [2].



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METHODS

Stable isotope composition of water appearances in Klodawa Salt Mine is monitored regularly since 1975 (one-two sampling campaigns per year). Here we report the results of the last two campaigns (January-March 2017 and January 2018), comprising altogether 29 samples. Thesamples were analyzed using two independent methods:

- conventional IRMS technique (Delta S machine) combined with prolonged CO_2-water equilibration (^{18}O) and high-temperature distillation followed by zinc reduction (^2H)
- direct analysis of distilled water samples (^2H, ^{18}O and ^{17}O) using Picarro L2140-*i* laser analyser.

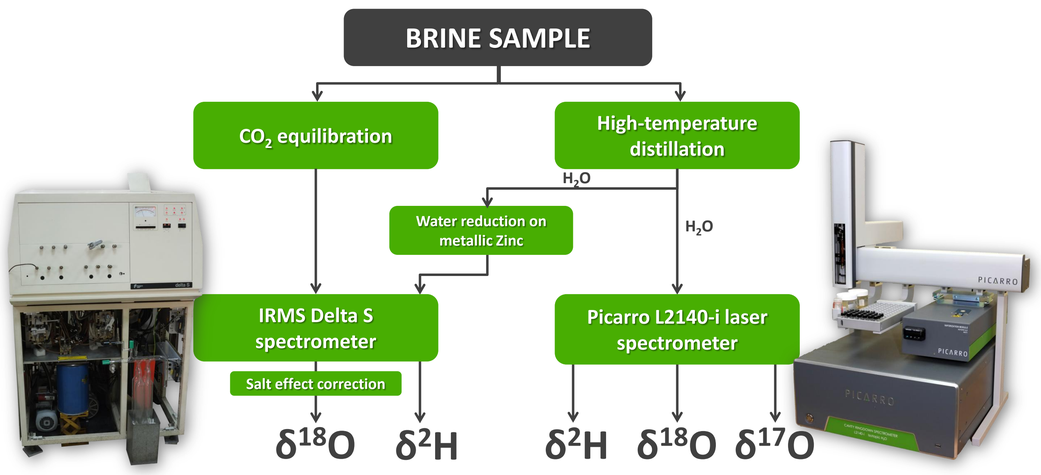


Fig. 3. Block-diagram of the methods applied in this study to analyse stable isotope composition of concentrated brines.

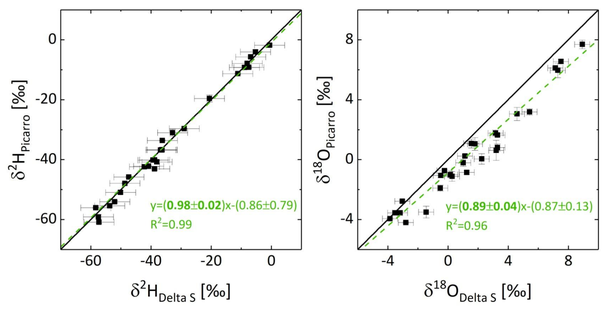


Fig. 4. Comparison of δ^2H and $\delta^{18}O$ measurements of Klodawa brines using two independent methods: (i) laser spectrometry (Picarro L2140-i laser analyser) and IRMS technique (Delta S machine).

RESULTS

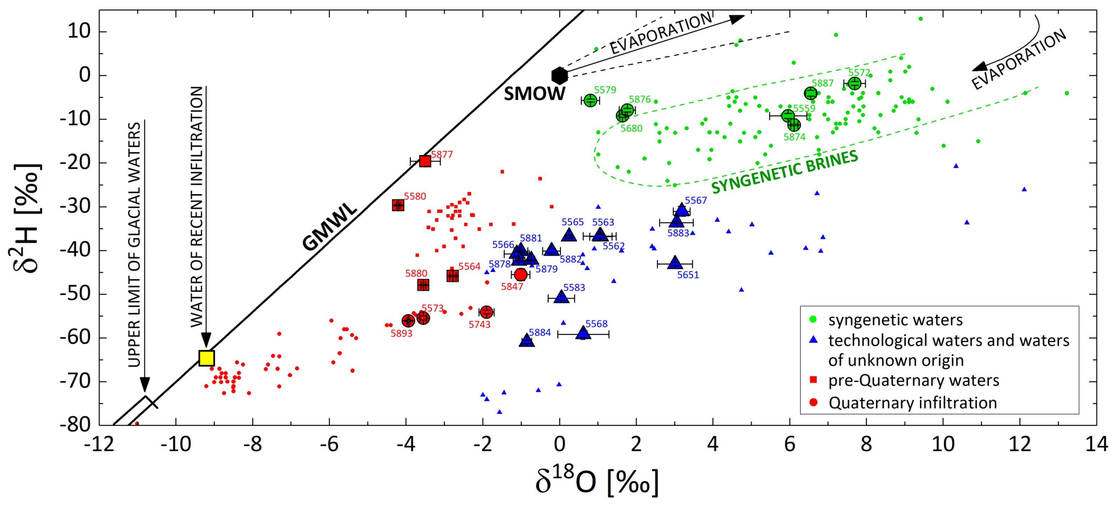


Fig. 5. Isotope characteristics of water appearances in the Klodawa Salt Mine. Small symbols - analyses using conventional IRMS technique (archive data: 1975-2016); large symbols - samples collected during 2017-2018 and analysed using Picarro L2140-i laser spectrometer.

Isotope characteristics of water appearances in the Klodawa Salt Mine are presented in Fig. 5. Three main groups of water were identified in the mine on the basis of their stable isotope composition. The first group (green symbols) represents syngenetic waters. They are of Zechstein age and represent different stages of the evolution of sea water during desiccation of shallow lagoons. Those waters are usually closed within salt pockets and occur in limited quantities; typically, their outflow stops after some period of time. Points representing stable isotope composition of these waters form characteristic "hook" on the δ^2H-$\delta^{18}O$ diagram.

The second group of points (red symbols in Fig. 5) represents waters posing certain risk for the operation of the mine. They are of meteoric origin and of different age. Most of them carry significant evaporation signature and at the present stage of knowledge it is difficult to decide whether the evaporation took place before infiltration or after their appearance in mine passages. Some of these waters were most probably recharged under climatic conditions significantly colder than those prevailing at present in central Poland. Other waters of this type most probably represent Holocene infiltration. There are also water appearances undoubtedly representing pre-Quaternary infiltration under significantly warmer climates than today.

The third group of points in Fig. 5 (blue symbols) represent technological waters and waters of unknown origin. Technological waters are local meteoric waters used inside the mine for various purposes and heavily enriched by evaporation. Some blue symbols represent waters appearing as drops on the connectors of pipelines and formed by condensation of atmospheric water vapor inside the mine.

The $\Delta^{17}O$-$\delta'^{18}O$ diagram shown in Fig. 5 reveals that these three groups of waters are characterized by different $\Delta^{17}O$ values, pointing to differences in their evaporation histories; highest $\Delta^{17}O$ values are observed for waters of meteoric origin whereas lowest $\Delta^{17}O$ values were measured for syngenetic brines. Interestingly, three samples of syngenetic brines (nos. 5579, 5876 and 5680) revealed intermediate $\Delta^{17}O$ values characteristic for technological waters and waters of unknown origin. Their position on δ^2H-$\delta^{18}O$ diagram suggest that those brines could possibly evolve under distinctly different environmental conditions (higher relative humidity) than other four syngenetic brines presented in Fig.5.

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CONCLUSIONS

- Stable isotope composition of concentrated brines constitute a powerful tool to trace the origin of water appearances in salt mines. Chemical composition of mine waters, although useful, cannot be used to distinguish between syngenetic (safe) and meteoric (potentially dangerous) water types occurring in such mines. Analyses of $\delta^{17}O$ and the secondary parameter $\Delta^{17}O$ provides additional constraints for this tool, delivering independent information about evaporation history of the analysed brine samples .
- Two independent analytical techniques employed in this study to measure stable isotope composition of concentrated brines revealed very good agreement for δ^2H, and some systematic differences for $\delta^{18}O$. The reasons for these differences are unclear at the moment and will be investigated further.

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